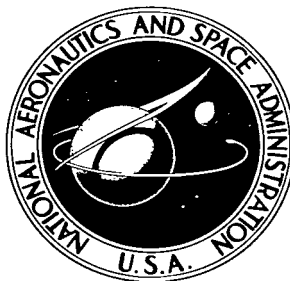


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THERMOPHOTOTROPISM IN CORTICATED ALKALINE EARTH TITANATES

by

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Goddard Space Flight Center*

and

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TAAG Designs, Inc.*



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SUMMARY

A comparison of acidic and acidic-to-basic impurity introduction on the thermophototropic behavior of the alkaline earth titanates is presented. The latter is a new method of introducing impurities into alkaline earth titanates which will be described here. It involves the synthesis of a photoactive titanate from a previously synthesized titanate or titanyl oxalate. This method gave a considerably enhanced absorptivity change for barium titanate, but proved to be much less effective for the titanates of calcium and strontium. In all cases the slurries were made alkaline with alkali metal hydroxides. For barium titanate the optimum alkalinity was obtained with 10 mole percent sodium hydroxide, which led to the conclusion that the phenomenon is a surface one in which the alkali metal oxide corticates the surfaces of the host crystals.

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INTRODUCTION

In the rather large group of photochemically active materials which have been categorized according to their optical properties, there exist many materials which change color when exposed to light of certain wavelengths. This phenomenon is referred to in its broadest sense as "phototropy."[†] The additional property of immediate color reversal with the removal of illumination is usually implied, but is not satisfied, *ipso facto*, by all phototropes. The alkaline earth titanates (with the exception of magnesium) provide an example. The speed of their change in color depends on their temperature. At room temperature they revert to their original color imperceptibly slowly. For instance, a decrease of 2 to 3 percent in the absorptivity of barium titanate at room temperature requires approximately 3 weeks. However, an exposed sample heated to 300°C returns to its original color in about 30 min. Therefore, a graph for barium titanate of the functional dependence of coloration on temperature gives a broad curve which extends from about zero to several hundred degrees centigrade. Consequently, the alkaline earth titanates are not phototropic in the same sense as organics and metal organics (which bleach at room temperature). Materials such as the alkaline earth titanates are called thermophototropes.

This paper reports a new procedure for the synthesis of a photoactive titanate from a previously synthesized titanate—a procedure which causes a considerably enhanced thermophototropic activity for the barium analog. It is appropriate to mention briefly other possible synthetic approaches. One is to dissolve a salt (impurity), usually a chloride, in distilled water and dilute this solution to such a volume that, when it is slurried with the titanate, a free flowing mixture is formed. Uniform distribution is then assured. A less convenient method involves wet or dry grinding of the impurity with the titanate. Identical procedures are suitable for use with the hydrated titanyl oxalates. Still another technique involves the co-precipitation of the impurity with a titanyl oxalate as part of the synthetic procedure.

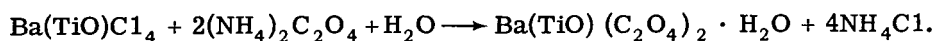
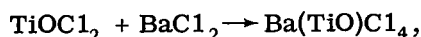
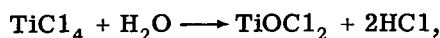
*Mr. Lepp did research work for this paper under contract NAS-5-2383 held by TAAG Designs, Inc., College Park, Maryland.

†Chalkley, L., Jr., "Phototropy," *Chem. Rev.* 6:217-280, 1929.

McNevin and Ogle* have reported qualitative results on the thermophototropic behavior of the alkaline earth titanates. The work was repeated here in order to establish quantitatively the extent of the photoresponse.

THE ADDITION OF IMPURITIES

Initially, barium titanate was slurried with the chloride impurities. The resultant mixture was dried, pressed, and fired for 1 hr at 1100°C. The titanates were synthesized via the oxalate process:



The conversion to a titanate was accomplished at 1100°C in 4 hr. Previous to firing, the hydrated titanyl oxalate was slurried with VOCl_3 , CrCl_3 , FeCl_3 , NiCl_2 , CuCl_2 , and ZnCl_2 at a level of 0.02 mole percent. After firing, samples of the titanate were reslurried separately with solutions of elements in the first transition series. The exposures were carried out under a mercury lamp, rich in the violet and near ultraviolet wavelengths, for 24 hr.

ABSORPTIVITY CHANGES FOR VARIOUS IMPURITIES

The results of the spectrophotometric studies are given in Table 1 for selected wavelengths. In an effort to find a scheme for the incorporation of impurities into the titanates, it seemed appropriate to look for synergisms. $\text{V}^{+3,5}$, Cr^{+3} , Fe^{+3} , and $\text{Mn}^{+3,+4}$ would be expected to predominantly replace Ti^{+4} , and Co^{+2} , Ni^{+2} , Cu^{+2} , and Zn^{+2} the alkaline earth metal. Thus it appeared that synergistic effects could be produced through simultaneous replacement of titanium and barium with cations carrying different ionic charges than that on the cation to be replaced. To this end, the alkali metals were chosen.

Table 1
Comparison of the Absorptivity Changes of BaTiO_3 with Acidic and Acidic-Basic Impurity Introduction.

Impurity Addition	Absorptivity Change (percent)			
	$\lambda = 0.4\mu$	$\lambda = 0.5\mu$	$\lambda = 0.6\mu$	$\lambda = 0.7\mu$
$\text{V}^{+3,+5}$	0	2	1	1
$\text{V}^{+3,+5} + \text{NaOH}$	17	56	49	39
Cr^{+3}	0	2	1	1
$\text{Cr}^{+3} + \text{NaOH}$	21	55	54	41
$\text{Mn}^{+3,+4}$	0	1/2	1/2	1
$\text{Mn}^{+3,+4} + \text{NaOH}$	8	26	32	30
Fe^{+3}	1	6	4	3
$\text{Fe}^{+3} + \text{NaOH}$	10	46	53	48
Co^{+2}	6	4	4	3
$\text{Co}^{+2} + \text{NaOH}$	6	10	16	25
Ni^{+2}	0	2	2	1
$\text{Ni}^{+2} + \text{NaOH}$	23	57	57	50
Cu^{+2}	2	8	4	0
$\text{Cu}^{+2} + \text{NaOH}$	10	41	47	40
Zn^{+2}	0	6	5	4
$\text{Zn}^{+2} + \text{NaOH}$	11	44	45	33

*MacNevin, W. M., and Ogle, P. R., "Phototropy of the Alkaline Earth Titanates," J. Amer. Chem. Soc. 76: 3846-3848, 1954.

The results are given in Table 1 for barium titanate with sodium hydroxide at the 10 mole percent level. They are compared with the corresponding sample prepared without sodium hydroxide. The hydroxide was normally added by reslurring the doped sample; vanadium was added simultaneously with sodium by means of the pervanadate. Broadly, therefore, Table 1 is a comparison of impurity activity in an acidic titanate with that in a basic titanate.

In an effort to find out whether the enhanced photoactivity was synergistic, barium titanate was mixed with sodium hydroxide alone. Figure 1 gives the reflectance curves for lithium, potassium, and sodium added to this mixture, from 0.35 to 0.7 μ . In this and the following figures the upper set of curves represents bleached samples and the lower set darkened samples. (In all the figures and tables the alkali metals were added at the level of 10 mole percent unless otherwise stated).

Figure 2 shows curve for barium titanate with the impurities V, Cr, Fe, and Mn and 10 mole percent sodium as before, and curves for the addition of sodium to the oxalate. Figure 3 is a comparison of the addition of sodium in hydroxide and carbonate forms. The enhanced photoactivity found for the carbonate cannot stem from the ease of calcination of sodium carbonate versus the ease of dehydration of sodium hydroxide, since the heat of formation of the former is about twice that of the latter. More likely, the enhancement can be attributed to a lack of decomposition, which gives a relatively dense electron environment.

In an effort to establish an approximate optimum concentration for sodium in barium titanate, the mole percent was varied from 2 to 30 while the samples were fired at 1100°C for 1 hr. The results are presented in Table 2, which shows that 10 mole percent is optimum. Samples with the optimum concentration for sodium were fired according to the schedules in Table 3. The optimum firing conditions turned out to be 1 hr and in the range 950-1100°C. Samples were made with lithium and potassium

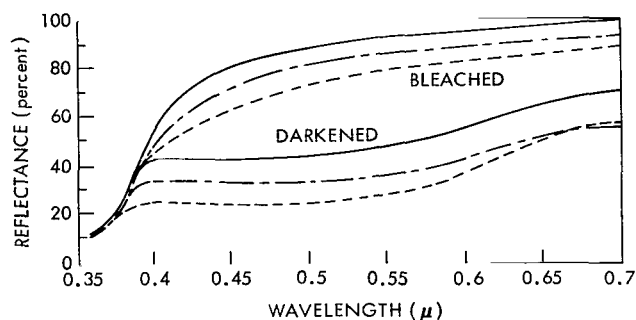


Figure 1—A comparison of the colorations of impure barium titanate with 10 mole percent additions of lithium (unbroken curve), potassium (dashed curve), and sodium (dotted curve).

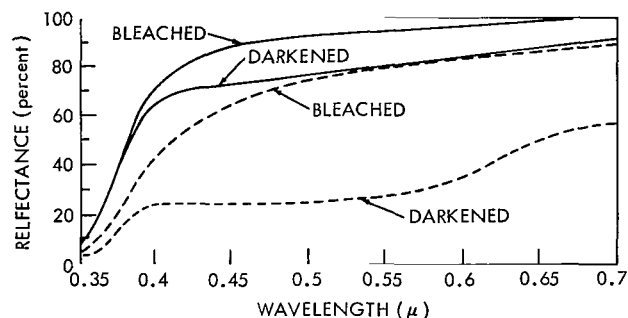


Figure 2—A comparison of the coloration of barium titanate with impurities and 10 mole percent of sodium added (unbroken curve) and barium titanate with impurities and 10 mole percent of sodium added.

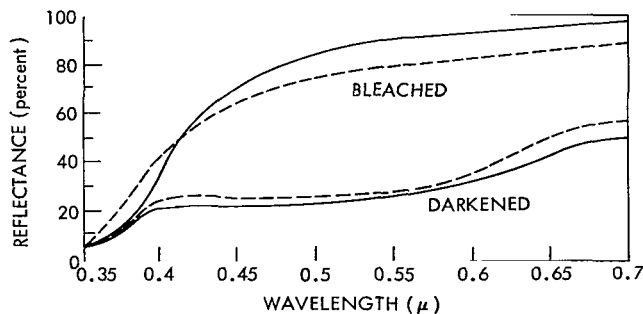


Figure 3—A comparison of the colorations of impure barium titanate with 10 mole percent additions of sodium hydroxide (broken curve) and sodium carbonate.

Table 2
Absorptivity Increments of Impure BaTiO₃ for the
Addition of Various Concentrations of Sodium.

Sodium Concentration (mole percent)	Absorptivity Change (percent)			
	$\lambda = 0.4\mu$	$\lambda = 0.5\mu$	$\lambda = 0.6\mu$	$\lambda = 0.7\mu$
2	6	30	26	17
5	9	50	47	36
10	15	50	49	37
15	9	55	52	37
20	9	52	51	37
30	8	48	47	35

Table 3
Absorptivity Changes of the BaTiO₃-Na₂O System
under Various Firing Conditions.

Conditions	Absorptivity Change (percent)			
	$\lambda = 0.4\mu$	$\lambda = 0.5\mu$	$\lambda = 0.6\mu$	$\lambda = 0.7\mu$
820°C for 1 hr	4	43	37	27
820°C for 3 hr	3	48	44	33
950°C for 1 hr	6	46	43	32
1100°C for 1 hr	7	45	42	31

additions, under the optimum conditions for sodium addition to barium titanate. These were compared with the sodium addition and the results are presented in Figure 1. Lithium addition gave the least response. Additions of sodium and potassium gave similar responses, but initially the sample with potassium colored more rapidly than that with sodium.

Identical synthetic procedures were carried out for calcium and strontium titanates, i. e., V, Cr, Mn, and Fe were added to the respective oxalates and this was followed by repeated additions of sodium to the titanate. After drying, the alkali metals were added and the mixtures were fired. The results are given in Table 4. Sodium and potassium increased the overall photoactivity in calcium but did not increase the photoactivity when added to strontium. Lithium inhibited the overall response. The impure sample was a commercial alkaline earth titanate which was included for the sake of comparison.

Table 4
Absorptivity Changes (percent) of Sodium-Doped CaTiO₃ and Sodium-Doped SrTiO₃ Systems at Various Wavelengths for the Introduction of Different Substances.

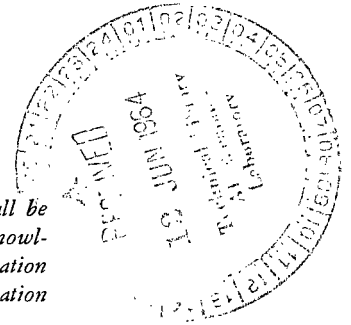
Addition	Absorptivity Change (percent)							
	CaTiO ₃				SrTiO ₃			
	$\lambda = 0.4\mu$	$\lambda = 0.5\mu$	$\lambda = 0.6\mu$	$\lambda = 0.7\mu$	$\lambda = 0.4\mu$	$\lambda = 0.5\mu$	$\lambda = 0.6\mu$	$\lambda = 0.7\mu$
Na	8	25	26	23	10	17	14	9
K	6	21	19	14	13	18	15	10
Li	-	-	-	-	9	13	11	8
Impure	6	13	13	9	19	17	14	8

CONCLUSION

The addition of sodium or potassium ions to impure barium titanate enhances the overall thermophototropic response. Since the level of addition was of such a magnitude that it precluded doping in the semiconductor sense, it seems reasonable to assume that the alkali metals are primarily surface active and do not predominately enter internal lattice positions. Consequently, they corticate the surfaces of the titanate host microcrystals. Lithium gave the least optical response and was temporarily the slowest with respect to the rate of coloration. For potassium coloration was nearly as great as for sodium and darkening proceeded more rapidly than for sodium during the initial stages. Since the ionic radius of potassium, 1.33Å, is nearly identical to that of barium, 1.35Å, the replacement of barium by potassium is favored over substitution by sodium (0.95Å). Since sodium can measurably increase the coloration, compared with potassium, it follows that Goldschmidt's Rules are only approximately obeyed for the surface-derived phenomenon of thermophototropism.

(Manuscript received December 5, 1963.)

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